

Nutrients, Suspended Sediment, and Pesticides in Water of the Red River Basin

Numerous stream sites were sampled in the Red River Basin during 1990–2004 (fig. 3). The number of samples collected at each site, however, often was not sufficient to characterize water-quality during all streamflow conditions. Streamflow was greater than average during some years and was less than average during others. The distributions of mean annual streamflows for 1990–2004 are shown in figure 4 for 22 USGS stream sites with continuous streamflow record. Long-term average streamflows for the period of record at each site also are shown. Streamflows at the four Red River sites exceeded the long-term average during 1990–2004. This is particularly evident at the Red River at Fargo (site 10), where 75 percent of the flows were greater than the long-term average. For 19 of the 22 streamflow sites in the basin, average annual streamflow exceeded the long-term average for the period of record at that site (fig. 4). Streamflows generally were less than the long-term average at the Bois de Sioux (site 7), Turtle River (site 37), and Pembina River (site 40) sites.

The importance of streamflow variability to this report is that streamflow can have a substantial effect on water chemistry. The high streamflows of the early 1990s are particularly important because they occurred during the growing season after pesticides were applied. Tornes and others (1997) reported that streamflows at most sites in the Red River Basin exceeded the 90th percentile of historical mean annual streamflows during 1993–95. The effect of these high streamflows was more apparent for southern and western streams where runoff was especially large. Suspended sediment and constituents related to the solid phase rather than the dissolved phase (total phosphorus, for example) typically are higher during higher flows.

Flooding can affect water quality in the spring when agricultural chemicals have been applied and when there is no crop cover on fields to hold soils in place. There were large floods in the basin in 1997 and 2001. The 1997 floods were the result of record high snow packs across the region, whereas the 2001 floods were the result of above average soil moistures in some areas of the basin (Macek-Rowland, 2001). The flat terrain of the Red River Basin and the shallowness of the channel can aggravate flooding. Samples collected during floods usually indicate much different stream quality than samples collected during low flow. Whereas floods can cause increases for some constituents, such as fertilizers and sediment, they also can have a diluting effect on other constituents, such as dissolved solids.

Nutrients

Nutrients, particularly nitrogen and phosphorus, have been identified as a source of the degradation of much of the Nation's surface water with respect to water quality (U.S. Environmental Agency, 2000). Although nutrients occur naturally in the environment, certain human activities can increase their transport to natural waters. Sources of nutrients include sewage effluent, lawn fertilizer, storm runoff, and certain agricultural practices such as livestock production and application of fertilizers.

Nitrogen occurs in several forms—ammonia, nitrite, nitrate, and as part of organic compounds. Ammonia plus organic nitrogen, also known as total Kjeldahl nitrogen (TKN), is a laboratory test for measuring the amount of organic nitrogen and ammonia in water. In most oxygenated surface water, nitrate is by far the most predominant ion because of the rapid oxidation of nitrite. Adverse human-health effects of large concentrations of nitrates (greater than 10 mg/L) in drinking water include methemoglobinemia, “blue-baby syndrome” in infants (U.S. Environmental Protection Agency, 1986).

Phosphorus is an essential nutrient for plant growth; however, if critical concentrations are exceeded, it may contribute to eutrophication. Eutrophication is characterized by an abundance of nutrients, decreases in dissolved oxygen, dense growth of algae, and an acceleration of the normal rate of ecological succession (Reid and Wood, 1976, p. 293).

Surface Water

Most of the sampling sites are primarily along the Red River (fig. 3) and in the Red River Valley Lake Plain (fig. 2). Another area of intense sampling is within the closed Devils Lake Basin (fig. 3). Few sites are in the Lake-Washed Till Plain or the Moraine. The limited distribution of sampling sites makes it difficult to generalize about the water quality for a certain physiographic area in the Red River Basin. Tornes and others (1997) found that nutrient concentrations generally were related to the physiographic area that a stream drains.

Because methods of collection and analysis are different, USGS data for nutrients in surface water and the nutrient data collected and analyzed by other agencies are discussed separately. All 23 USGS sites meeting selection criteria are included in figure 5. Nitrite plus nitrate concentrations ranged from 0.02 to 5.2 mg/L in samples from USGS stream sampling sites; concentrations between the 10th and 90th percentile are displayed in fig. 5A. Median nitrite plus nitrate concentrations ranged from 0.05 to 0.67 mg/L.

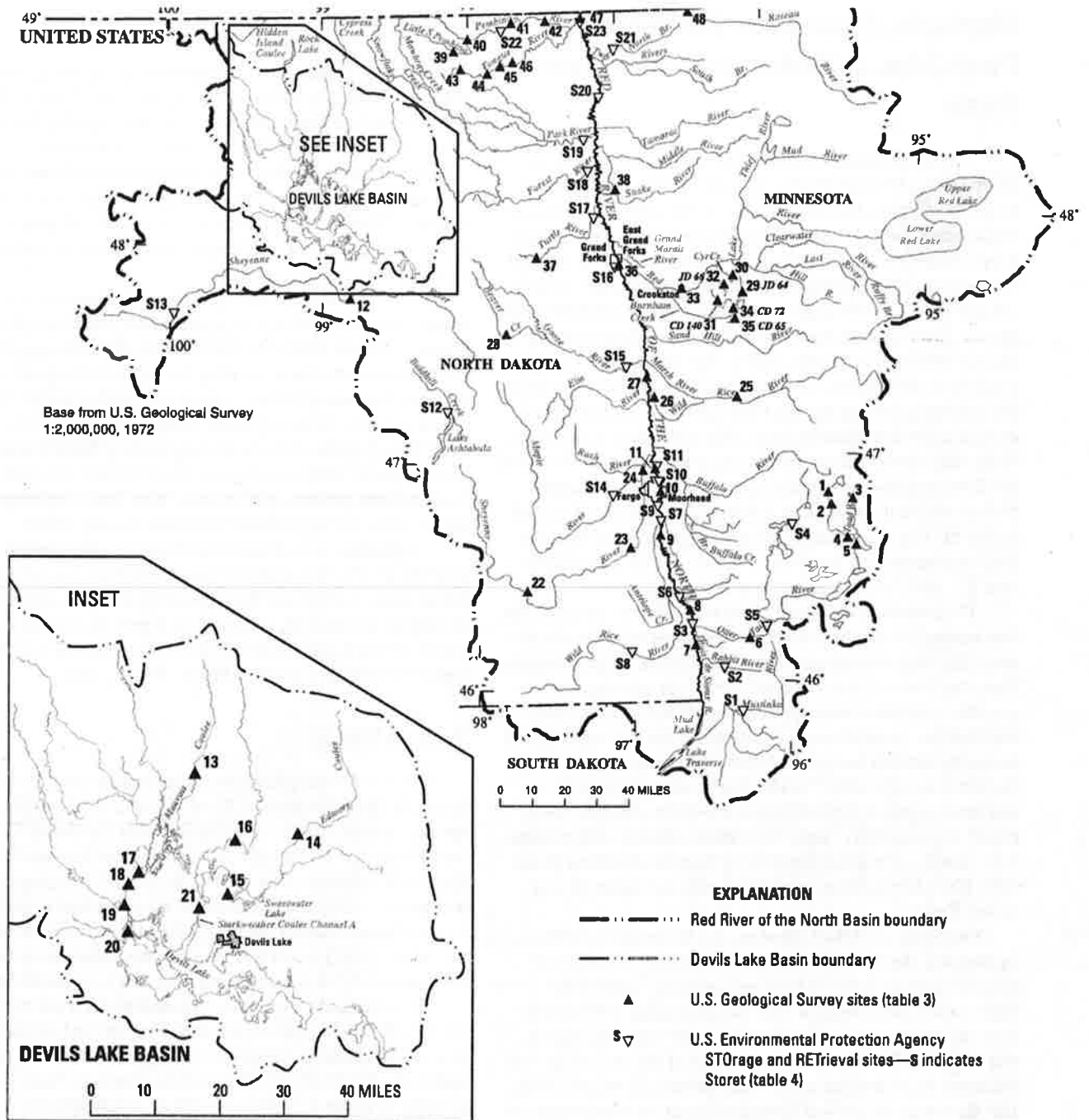


Figure 3. Surface-water sampling sites in the Red River of the North Basin, 1990–2004.

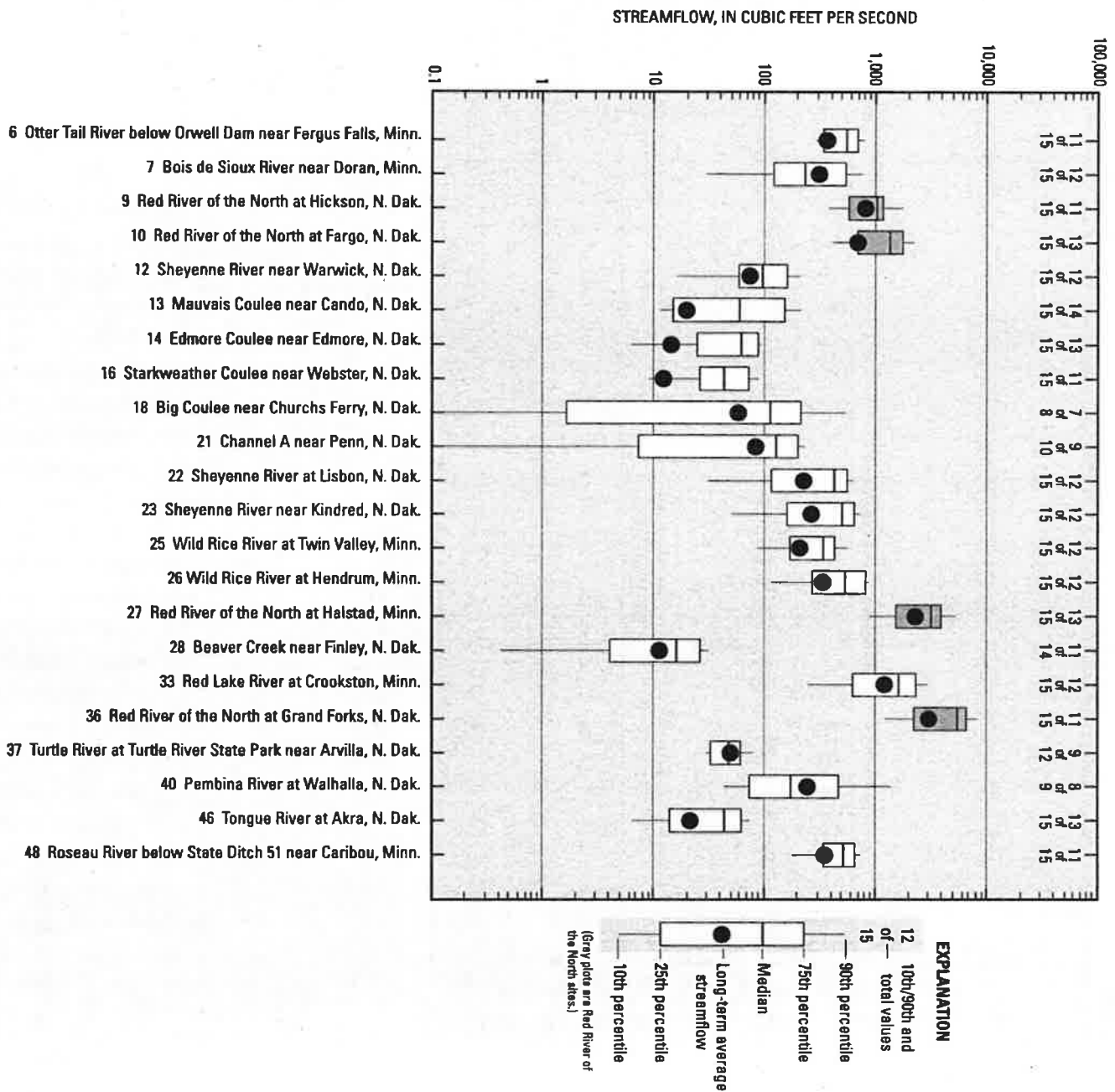


Figure 4. Distribution of mean annual streamflow for 22 U.S. Geological Survey sites with continuous streamflow record in the Red River of the North Basin, 1990–2004.

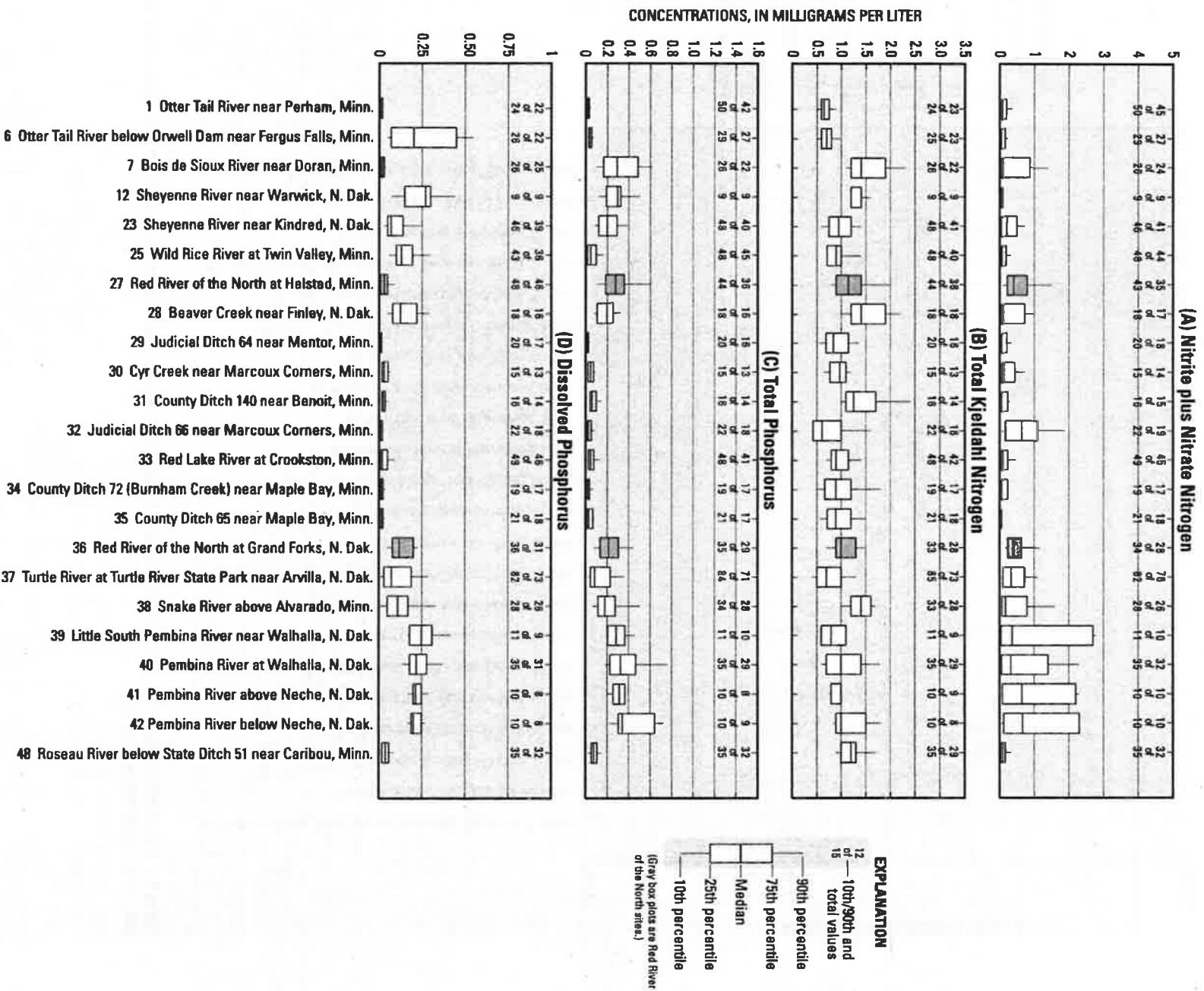


Figure 5. Distribution of (A) nitrite plus nitrate nitrogen, (B) total Kjeldahl nitrogen, (C) total phosphorus, and (D) dissolved phosphorus concentrations for 23 selected U.S. Geological Survey stream sites in the Red River of the North Basin, 1990–2004.

The most noticeable pattern in nitrite plus nitrate concentrations across the basin is the high concentrations in samples from the Little South Pembina and Pembina River (sites 39, 40, 41, and 42, fig. 3) compared to concentrations in samples from other Red River Basin sites (fig. 5A). Although these sites are located in the Drift Prairie and Red River Valley Lake Plain, they mainly drain the Drift Prairie physiographic area. Ternes and others (1997) found that streams draining the Drift Prairie had much higher concentrations of nitrate than other streams in the basin. The Drift Prairie physiographic area drains some of the steepest agricultural land in the basin, which probably contributed to more rapid runoff of nutrients (Ternes and Brigham, 1994). The Bois de Sioux River (site 7, fig. 3), the Red River at Halstad (site 27, fig. 3), and Judicial Ditch 66 near Marcoux Corners (site 32, fig. 3) had slightly higher concentrations than nearby sites. The main-stem site at Halstad probably is influenced by municipal and industrial wastes from the cities of Fargo and Moorhead (Ternes and Brigham, 1994). All nitrite plus nitrate concentrations in samples from USGS stream sites between 1990–2004 were less than the drinking water standard of 10 mg/L (U.S. Environmental Protection Agency, 1996). Nitrite plus nitrate concentrations less than 10 mg/L are not considered a threat to human health.

Ammonia concentrations typically were low at most sites where data were available; therefore the TKN results likely are mostly organic nitrogen. TKN concentrations in samples from USGS sites meeting selection criteria ranged from 0.1 to 7.5 mg/L; concentrations between the 10th and 90th percentile are shown in figure 5B. Median TKN concentrations in samples from USGS sites ranged from 0.61 to 1.4 mg/L; TKN concentrations were highest at Bois de Sioux (site 7), Beaver Creek near Finley (site 28), County Ditch 140 near Benoit (site 31), and Snake River at Alvarado (site 38). No regional pattern is apparent with these TKN concentrations, which were found in samples from different areas of the basin. Excessive organic nitrogen in water may indicate contamination from human and animal waste.

Total phosphorus concentrations in water samples from USGS stream sites ranged from less than 0.005 to 4.14 mg/L; concentrations between the 10th and 90th percentile are shown in figure 5C. Median total phosphorus concentrations ranged from 0.018 to 0.345 and were highest at the Bois de Sioux (site 7, fig. 3), Sheyenne River (site 12, fig. 3), Red River (sites 27 and 36, fig. 3), Little South Pembina River (site 39, fig. 3), and Pembina River (sites 40, 41, and 42, fig. 3) sites. Some Red River sites are near or downstream from wastewater effluent, which may explain high total phosphorus concentrations compared to those in samples from sites further upstream.

Samples from the Pembina River sites had higher total phosphorus concentrations than those from nearby sites. Soil characteristics or agricultural practices and steep topography most likely cause more phosphorus to be transported to the stream. In addition, Pembina River sites drain the Drift

Prairie physiographic area, an area that had higher phosphorus concentrations than other Red River Basin sites in a previous study (Ternes and others, 1997).

Dissolved phosphorus concentrations at the USGS stream sites ranged from 0.003 to 4.13 mg/L; concentrations between the 10th and 90th percentile are shown in figure 5D. Median dissolved phosphorus concentrations ranged from 0.01 to 0.28 mg/L. Samples with high median dissolved phosphorus concentrations were from the Sheyenne River near Warwick, N. Dak. (site 12, fig. 3), Little South Pembina (site 39, fig. 3), and Pembina River sites (sites 40, 41, and 42, fig. 3). Because no large urban areas are located upstream from these sites, it is suspected that agricultural practices, such as livestock operations, are affecting water quality at some of the sites.

Data for nutrients in stream water from STORET were available for many sites. Results from 23 of these sites are shown in figure 6 and are discussed below. Nitrite plus nitrate concentrations for selected STORET sites ranged from less than 0.005 to 7.7 mg/L; concentrations between the 10th and 90th percentile are displayed in figure 6A. The highest median concentration occurred at the Red River of the North near Harwood, N. Dak. (site S11, fig. 3). This site is downstream from Fargo and Moorhead wastewater treatment plants, which may explain the higher nitrite plus nitrate concentrations.

For the STORET sites, TKN concentrations ranged from 0.234 to 2.38 mg/L; concentrations between the 10th and 90th percentile are shown in figure 6B. Median TKN concentrations ranged from 0.57 to 1.0 mg/L. TKN concentrations were highest at Mustinka River (site S1), Rabbit River (site S2), and Two Rivers (site S21). Relatively low TKN concentrations were found in samples from the Otter Tail River (site S5), Red River (sites S6, S11, S16, and S23), and Pembina River (site S22). Low concentrations of TKN occurred at all Red River sites except at the Bridge on Main Avenue at 3rd Street in Moorhead, Minn. (site S10). This pattern of low concentrations on the mainstem sites was not expected and was not observed from 1970–90 (Ternes and Brigham, 1994). The data for the Red River of the North Bridge on Main Avenue at 3rd Street was analyzed by a different lab during 1990–2004 than the other Red River sites in the graph (fig. 6B). This emphasizes the importance of documenting quality assurance procedures and considering these when evaluating data from numerous sources, such as those from STORET.

Total phosphorus concentrations in samples from selected STORET stream sites ranged from 0.018 to 1.44 mg/L; concentrations between the 10th and 90th percentile are shown in figure 6C. The range in median total phosphorus concentrations was 0.05 to 0.30 mg/L. The highest median concentrations were detected at the Pembina River site S22. Concentrations at Pelican River (site S4) were substantially lower than at other STORET sites (fig. 5C). A large number of samples (149) were analyzed at this site and, therefore, this is probably a valid difference and not an artifact of different sampling schemes.

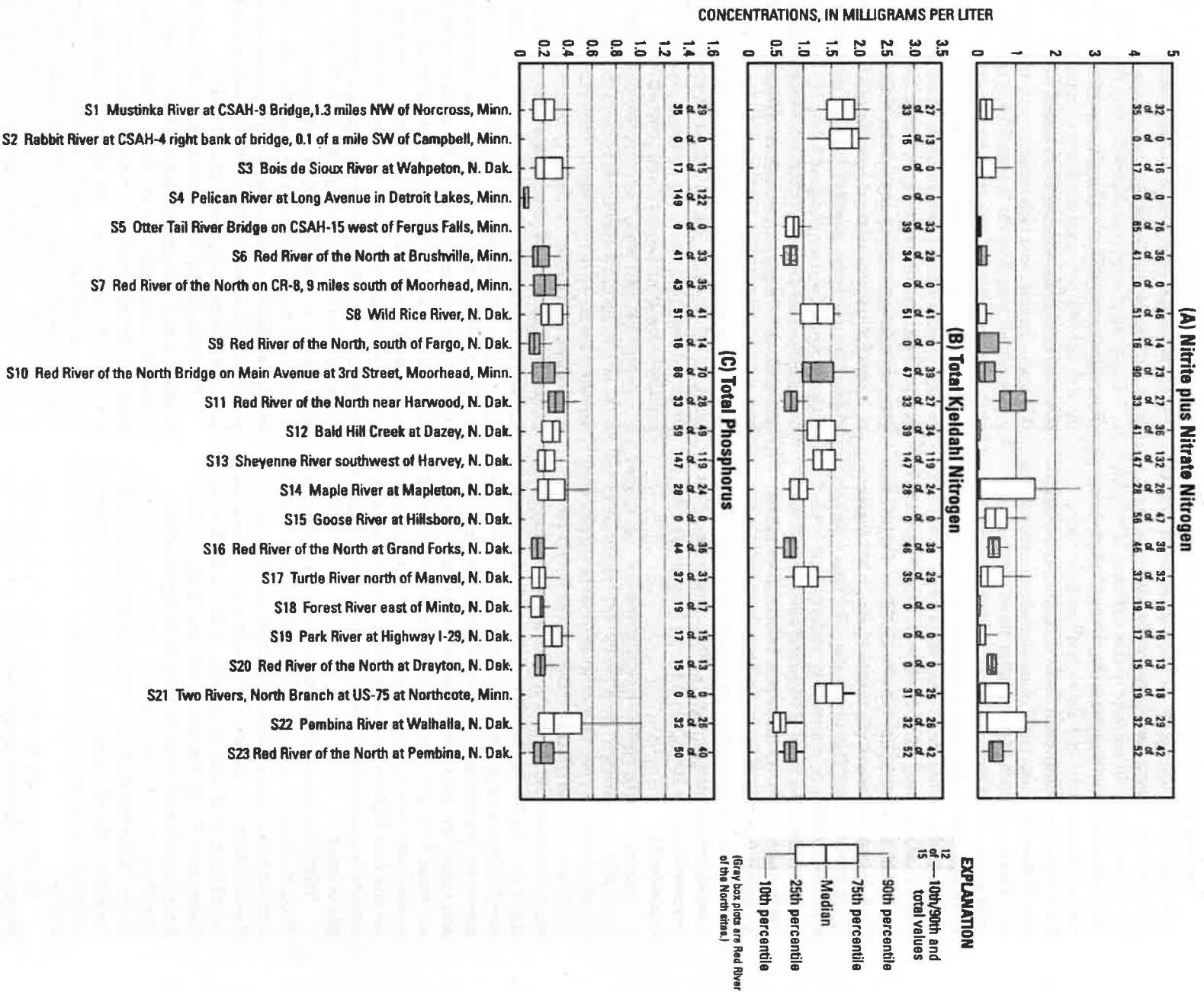


Figure 6. Distribution of (A) nitrite plus nitrate nitrogen, (B) total kjeldahl nitrogen, and (C) total phosphorus concentrations for selected U.S. Environmental Protection Agency STORE and RETRIEVAL stream sites in the Red River of the North Basin, 1990–2004.

Ground Water

The form of nitrogen most frequently analyzed in ground water samples was nitrate; there were several reasons for this. Nitrate is a dissolved form, the analysis is reasonably easy, and there is the Maximum Contaminant Level of 10 mg/L, to which concentration values can be compared. Bacterially mediated reactions can reduce nitrate to other forms of nitrogen under anoxic conditions, but these forms are not typically analyzed. Therefore, nitrogen contamination in ground water may affect a wider area, but this would not be apparent when water samples are analyzed for only nitrate.

Reported nitrate concentrations (as nitrogen) in ground water from North Dakota counties ranged from less than 0.023 to 113 mg/L (fig. 8) from 1990 through 2004. About 15,000 samples from North Dakota counties from 1990 through 2004 were analyzed for nitrate. Samples from Sheridan County had the highest median nitrate concentrations, whereas samples from Rolette County had the lowest median concentrations. Sheridan County is located on the far western side of the basin in the Drift Prairie physiographic area and the land use is mainly cropland and grazing (fig. 2). Rolette County is in the far northwestern part of the basin and also is located in the Drift Prairie physiographic area, however, the land use is mixed with some woodland and cropland (fig. 2).

Nitrate concentrations in 613 samples from ground-water wells in Minnesota counties ranged from less than 0.005 to 133 mg/L (fig. 9). The highest concentrations were detected in Marshall and Otter Tail Counties. Very low median concentrations (most values were non-detectable) occurred in Itasca, Kittson, Norman, Stevens, and Wilkin counties. Ground-water nitrate data was not available for Big Stone, Clay, Lake of the Woods, and Roseau Counties. The samples with the highest median ground-water nitrate concentrations were collected from wells in Marshall, Otter Tail, and Polk Counties (fig. 9).

Fertilizer applications (table 1) were examined to determine if there was a correlation between these and nitrate concentrations in ground water (figs. 8 and 9). With the exception of Cavalier County, the North Dakota counties that had the highest fertilizer applications (Barnes, Cass, Richland) as shown by acres treated did not correspond to the North Dakota counties that had the highest ground-water nitrate concentrations (Ransom, Sheridan, and Traill). There appears to be little correlation between fertilizer applications (table 1) and nitrate concentrations in ground water in North Dakota Counties (fig. 8).

For Minnesota counties, Marshall, Norman, and Polk had the highest fertilizer applications as shown by acres treated with commercial fertilizers in table 1. Otter Tail County had considerably more acres treated with manure (table 1) than other Minnesota counties. Marshall, Otter Tail, and Polk counties also had the highest nitrate concentrations in ground-water wells when compared to other counties in the basin (fig. 9). Norman County did not have high ground-water nitrate

concentrations, but only three wells were sampled in Norman County and it is possible that these wells were not representative of the general water quality of ground water in Norman County.

The lack of correlation for some counties between fertilizer applications and ground water nitrate concentrations in wells may be because the nitrate comes from another source. High nitrate concentrations in ground water also may be an indication of contamination by sewage or agricultural wastes (Drever, 1988, p. 70). Most investigators have attributed high nitrate concentrations in rural wells to drainage from nearby barnyards or septic systems (Hem, 1992).

The lack of correlation for some counties between fertilizer applications and ground water nitrate concentrations in wells also may be due to differences in surficial geology. Much of the ground water in Otter Tail and Becker Counties is in unconfined, shallow aquifers and susceptible to contamination (Tornes and Brigham, 1994). Shallow ground water is at risk for nitrate contamination because nitrate ions are highly soluble in water, susceptible to leaching, and move freely through soil along with water (Campbell and others, 2004, p. 152). Areas with the highest risk for nitrate contamination generally have high nitrogen inputs, well-drained soils, and a high ratio of cropland to woodland (U.S. Geological Survey, 1999). Contamination of shallow ground water may be a warning to alert populations of potential future risks from consumption of water from deeper wells in these aquifers (U.S. Geological Survey, 1999).

Three additional sources of ground-water quality data were reviewed for this report. These data were collected through the MDNR, MDA, and MPCA's GWMAP. The MDNR collected ground-water samples in the Red River Basin in Minnesota. These samples were collected during 1992 and 1993 and analyzed for phosphorus, phosphate, nitrite, and nitrate. Data were not available by county. Nitrate values for 178 samples collected ranged from less than 0.10 to 14.7 mg/L. The MDA also collected some ground-water samples in Minnesota in 2004. Electronic files for these data were provided to the MPCA from MDA (Catherine O'Dell, Minnesota Pollution Control Agency, written commun., 2006). Nitrite plus nitrate concentrations ranged from zero to 6.27 mg/L for samples collected from 18 wells. The MPCA collected large amounts of ground-water quality data through GWMAP. Baseline data were collected from 1992–1996 and included metals, major ions, field properties, nitrate, and total phosphorus. Of the 124 wells sampled in the Red River Basin, 7 had water with detectible concentrations of nitrate. The detected concentrations generally were from water collected from wells in the buried Quaternary aquifers and concentrations for these seven wells ranged from 0.5 mg/L to 2.6 mg/L. More information on the GWMAP data is available at <http://www.pca.state.mn.us/water/groundwater/gwmap/gwbaseline.html>.

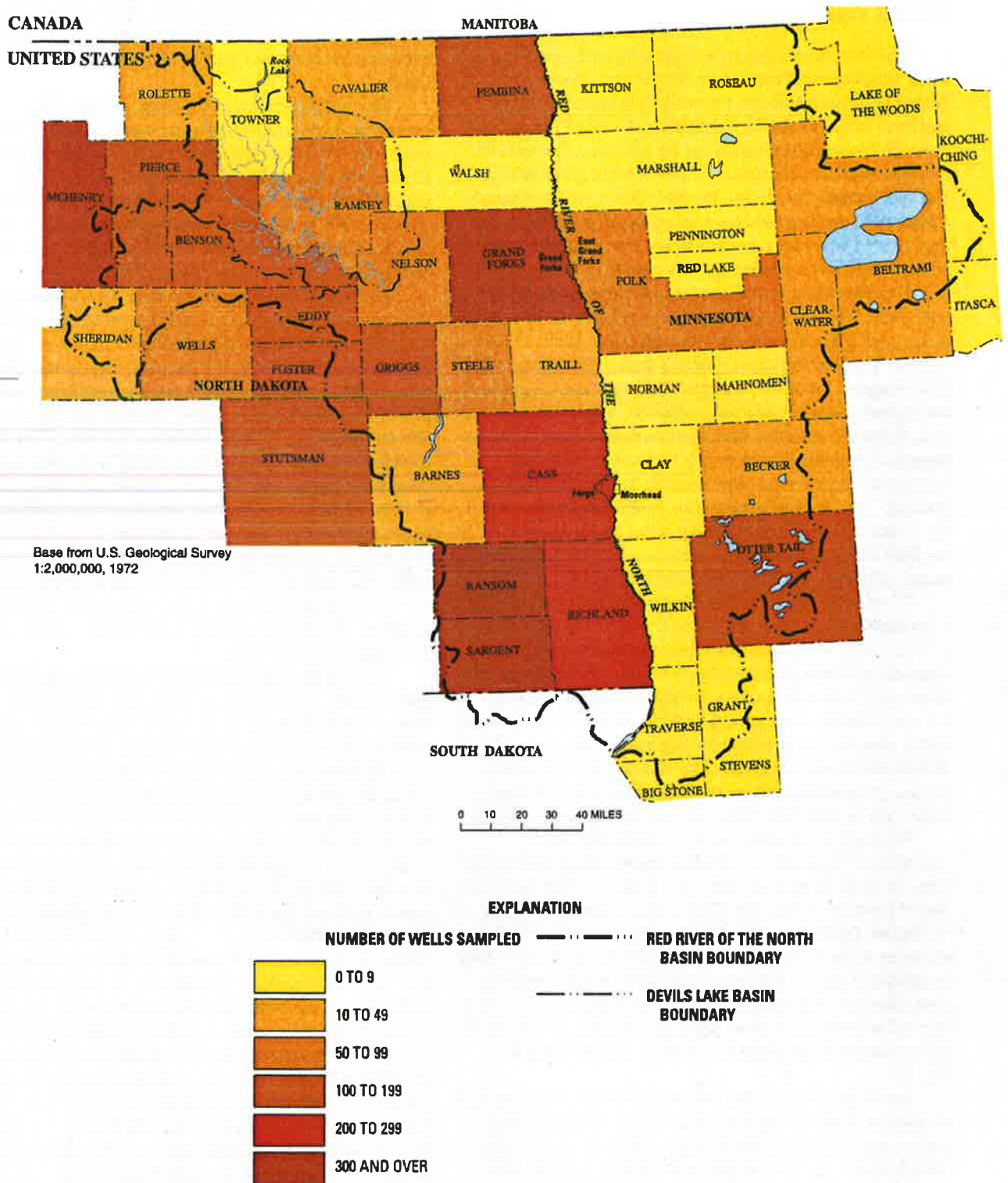


Figure 7. Numbers of wells sampled, by county, during 1990–2004 in the Red River of the North Basin.

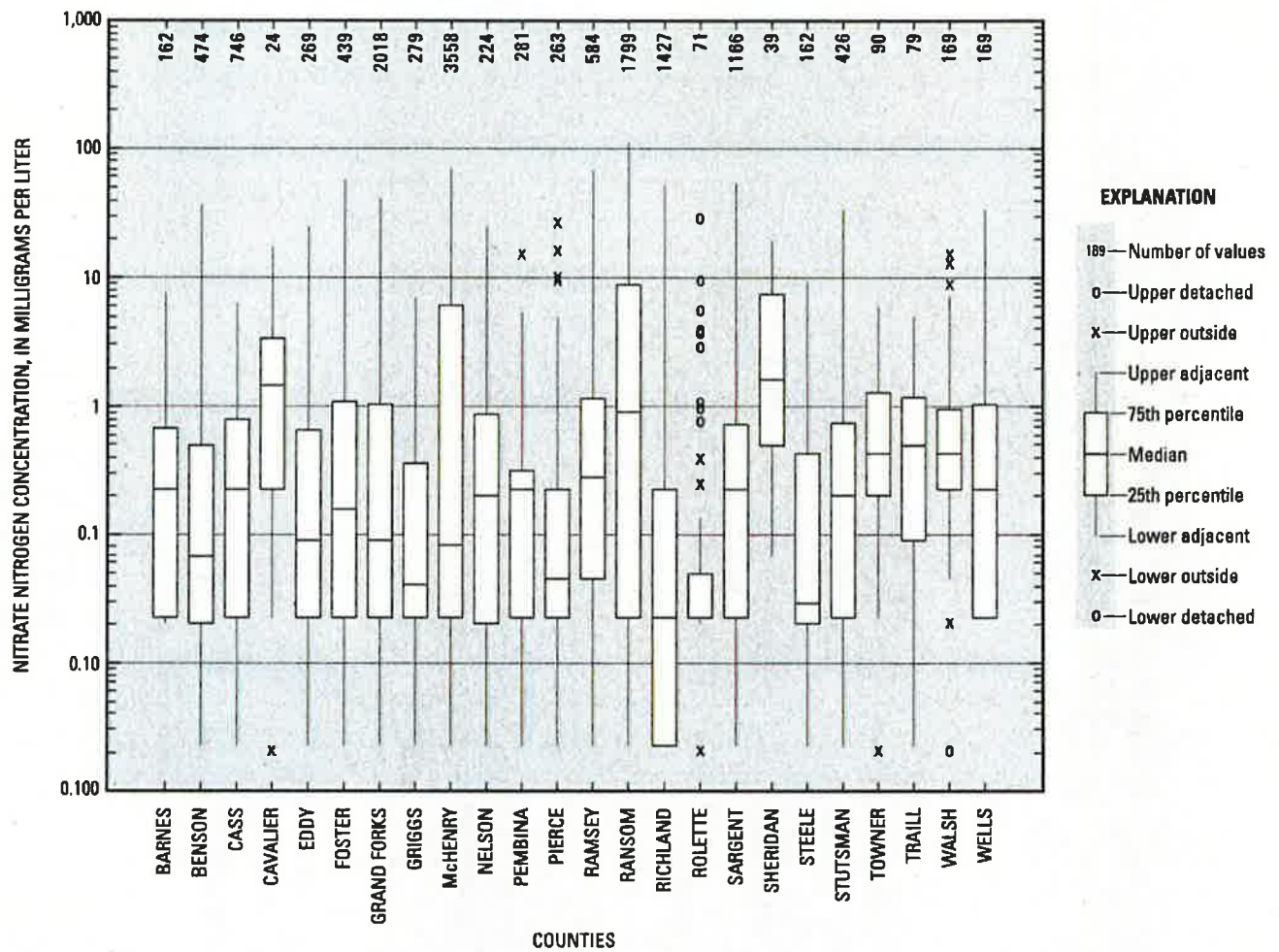


Figure 8. Distribution of nitrate nitrogen concentrations in water from wells in North Dakota counties in the Red River of the North Basin, 1990–2004.

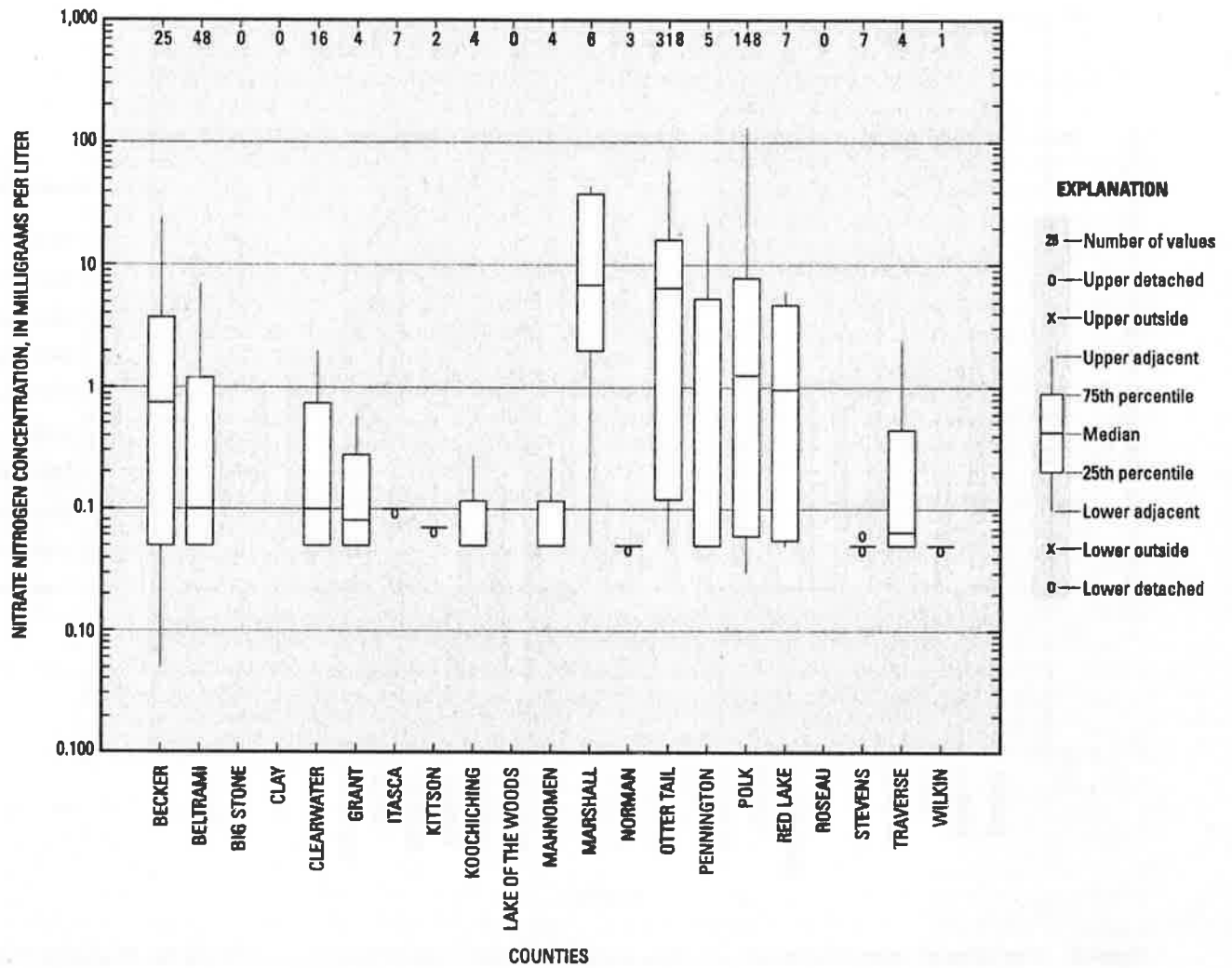


Figure 9. Distribution of nitrate nitrogen concentrations in water from wells in Minnesota counties in the Red River of the North Basin, 1990–2004.

Suspended Sediment

Sediment may be naturally transported to streams from soil erosion of stream banks and upland areas, especially during floods and other major hydrologic events. Sediment transport also can be increased by human activities such as construction, agriculture, and channel modifications. The increase in soil transport to streams from these human activities can have detrimental effects on water quality. For example, sediment in water can absorb, reflect, and scatter solar radiation and increase water temperatures, which may stress aquatic organisms and create conditions favorable to disease in fish populations (Christensen and others, 2006). The sediment smothers rooted vegetation and adversely affects benthic (bottom dwelling) organisms. In addition, the suspended sediment transported by streams can carry and deposit hydrophobic contaminants (those that do not dissolve in or combine with water) into reservoirs and lakes.

Certain solute-sediment interactions, such as those between sediment and organic compounds, for example, make suspended sediment an important water-quality factor. There are two different measures of solid material in a water sample, suspended-sediment concentration (SSC) and total suspended solids (TSS). SSC represents suspended solid-phase material in a water sample. SSC is determined by measuring the dry weight of all the sediment of a known volume of water-sediment mixture, unlike TSS in which the data are produced from a subsample of the original (Gray and others, 2001).

The differences between SSC and TSS are discussed in detail in Gray and others (2001) and a discussion of the difference between these two measures of suspended material in Minnesota and North Dakota are compared by Tornes and Brigham (1994). Tornes and Brigham demonstrated that TSS underestimates suspended-material content by more than a factor of two. The North Dakota Department of Health recently (about 2004) began analyzing the entire sample volume for TSS in order that TSS values from that laboratory would better correlate to SSC values from the USGS (Mike Ell, oral commun., January 22, 2007).

U.S. Geological Survey SSC data were available for the Red River Basin from 48 sites in Minnesota and 31 sites in North Dakota. In addition, data were available from 10 sites on the Red River, which forms the border between the two states.

Figures 10 and 11 show the distribution of SSC for all of the sites in the Red River Basin that meet the selection criteria of more than eight samples during at least two sampling seasons. Figure 10 shows the results of analysis of samples sites upstream from Grand Forks, N. Dak., and figure 11 shows the results of analysis of samples from Grand Forks and sites downstream. Median SSC ranged from about 4 mg/L at Otter

Tail River at Pine Lake Outlet near Perham, Minn. (fig. 10, site 2), to 706 mg/L at Pembina River at Walhalla, N. Dak. (fig. 11, site 40). Median concentrations in the Red River ranged from 52 mg/L at the Red River of the North below Wahpeton, N. Dak. (fig. 10, site 8) to 206 mg/L at Red River at Pembina, N. Dak. (fig. 11, site 47). Median concentrations were lowest at the Otter Tail River sites (fig. 10, sites 2, 5, and 6) and Turtle River (fig. 11, site 37). The highest SSC generally were found in the Pembina River (fig. 11). SSC in the Pembina River at Walhalla, N. Dak. (fig. 11, site 40) ranged from 10 mg/L to 3,290 mg/L. Tornes and Brigham (1994) also noted that the highest concentrations in the Pembina River 1970–1990 ranged from 3 mg/L to nearly 7,000 mg/L. SSC in the Tongue River above Renwick Dam (site 45) also are relatively high, but some sediment settles out behind the dam so that downstream concentrations from site 46 are lower (fig. 11).

The fine clay and silt lake-plain sediments in the Red River Valley are easily suspended and tend to stay in suspension even during relatively low-flow conditions (Paakh and others, 2006). The higher concentrations of suspended sediment in the Pembina River may be due to the steeper topography in the Pembina watershed (Tornes and Brigham, 1994) and erodible stream channels (Stoner and others, 1998). However, topography in the upper reaches of the Otter Tail watershed also is steeper than that in the Red River Valley Lake Plain and, therefore, topography is not the only factor affecting sediment transport. The transport of suspended sediment to surface water is likely due to a number of factors. Land use (fig. 2) in the Pembina watershed is mostly cropland and some woodland, compared to a combination of cropland, forest, and woodland in watersheds, such as the Otter Tail River, in which lower SSC are found. The Otter Tail River and other sites with lower SSC flow through numerous lakes and reservoirs, resulting in lower SSC concentrations downstream (Stoner and others, 1998). In addition, SSC in the Otter Tail and Wild Rice Rivers have larger grain size (a higher percentage of sand-to-silt) than other sites in the basin (Tornes and others, 1997) and these larger grain sizes are not as easily suspended as smaller grain sizes and would tend to settle onto the streambed. Agricultural land use and stream modification for irrigation and drainage also can influence sediment transport to streams.

In addition to the differences stated above, SSC generally was higher in samples from main-stem Red River Basin sites upstream from Grand Forks than in samples from other tributary sites upstream from Grand Forks (fig. 10) because of the cumulative effect of streamflow at main-stem sites. However, the concentrations at the Red River at Grand Forks (site 36) and Pembina (site 47) generally are no higher than concentrations at surrounding tributary sites (fig. 11).

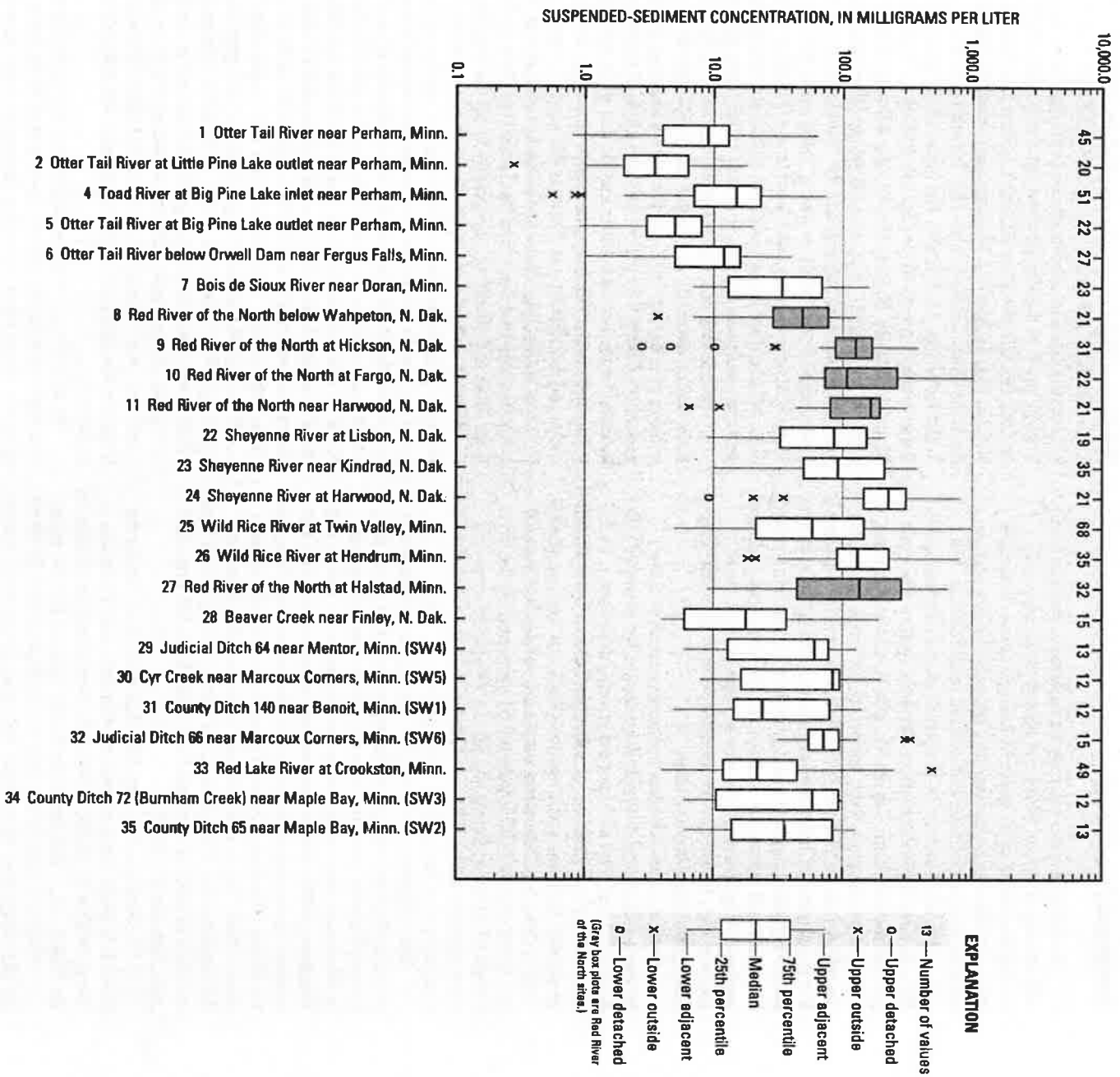


Figure 10. Distribution of suspended-sediment concentrations for stream sites in the Red River of the North Basin upstream from Grand Forks, North Dakota, 1990–2004.

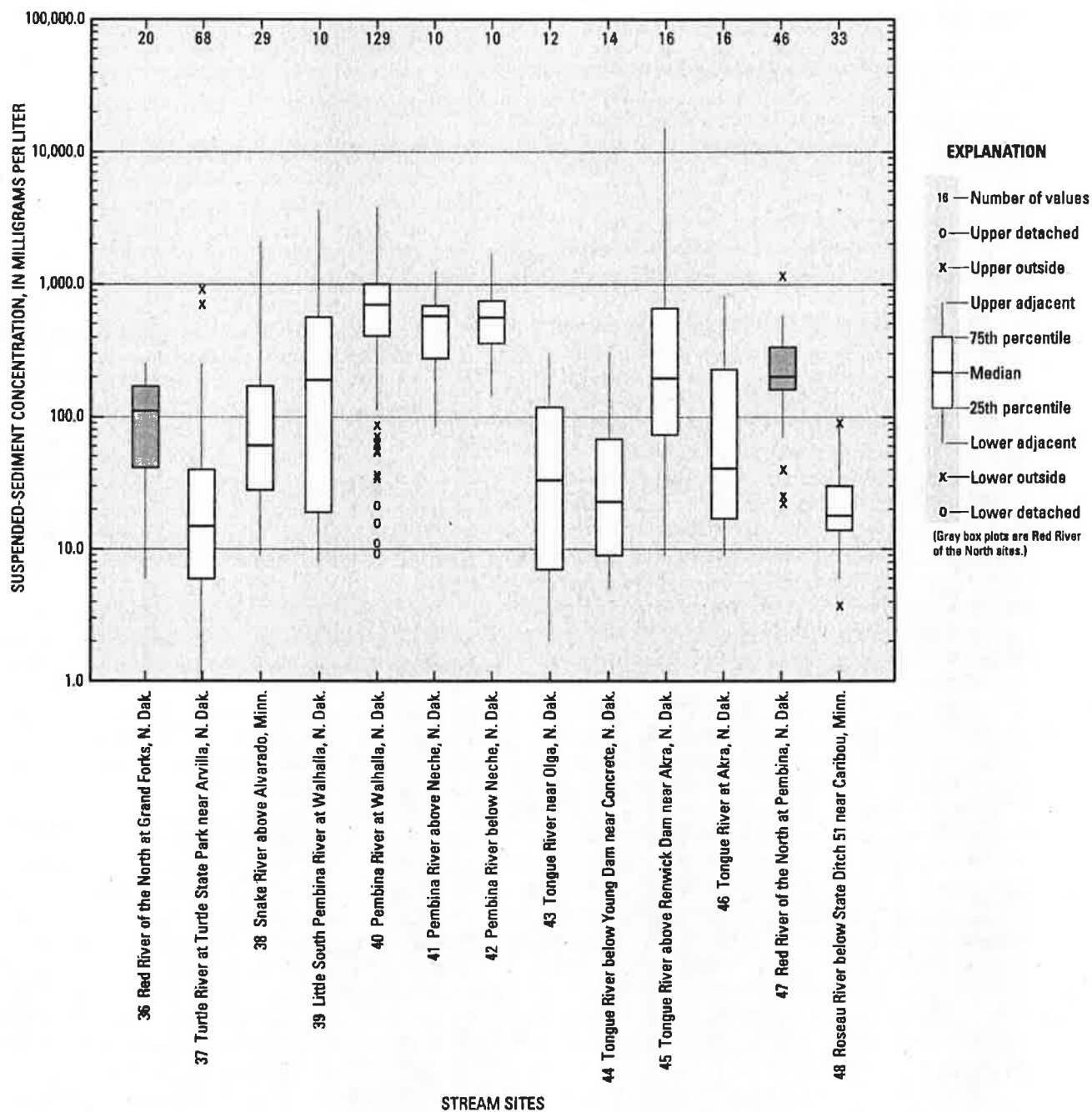


Figure 11. Distribution of suspended-sediment concentrations for stream sites in the Red River of the North Basin at Grand Forks, North Dakota and downstream, 1990–2004.

Pesticides

Pesticides include many chemicals that are commonly used to control weeds, insects, and other pests. The use of pesticides has many benefits, including increased food production, but also has adverse effects, including the adverse effect on water quality. Although pesticides seldom are detected in water at concentrations greater than human health guidelines, the likelihood of pesticide concentrations exceeding a human-health benchmark in streams is greatest for those streams draining urban or agricultural watersheds (Gilliom and others, 2006).

The occurrence of pesticides in aquatic systems may result from past or present uses in the watershed from agricultural land; golf courses; lawn and garden pest control in urban areas; forest management; maintenance of rights-of-way, for example, to control weeds on railroads; or atmospheric transport from other areas. The movement of pesticides through the aquatic system can be affected by aqueous solubility and adsorption to soils; vapor pressure; lipophilicity or the tendency of a chemical to dissolve in lipids; loss mechanisms, such as biological or chemical degradation and volatilization; and environmental factors, such as runoff events and topography (Tornes and Brigham, 1994). The transport of chemicals to surface water also is affected by some agricultural best management practices, such as vegetated buffers, and other conservation practices.

Pesticide data available for the Red River Basin is the result of several different studies and sampling programs. These studies and programs were designed for specific purposes and may be site specific; therefore, data for certain pesticides are available for only a few sites. This is not an indication that a particular pesticide was not used in other areas of the basin, but that there was no sampling program in those other areas. There is considerable difference in the sampling schemes between agencies in Minnesota and North Dakota. Pesticide data for surface water in the STORET data base are available for more sites in North Dakota than in Minnesota, but many of the North Dakota sites have fewer samples. The data in this report are limited to synthetic organic pesticides. Inorganic compounds used as pesticides, such as copper, are not included.

Surface-water and ground-water pesticide data are discussed separately. Red River Basin ground-water sites in NWIS or STORET from 1990 through 2004 do not have enough pesticide data to perform statistical analyses for trends and none of the sites met selection criteria. Most of the pesticide data available for the Red River Basin are from programs in which many sites over a large geographic area are sampled only once and this especially is true for ground-water surveys. Although these data cannot be used to detect trends at a particular site, they can be examined to determine which pesticides have been detected in surface and ground water and to assess potential contamination of water in the basin. Analyses in which pesticides are not detected because concentrations

are below the reporting levels also are important in assessing contamination of water in the basin.

Surface Water

The NWIS data base was searched for all pesticide data collected from surface water during 1990–2004 in the Red River Basin. More than 120 different pesticides or metabolites were present in the data base. Pesticide data that met the selection criteria established in the Methods section of at least 8 samples over 2 years were found for 12 sites—2 sites on the Red River, 3 sites in Minnesota, and 7 sites in North Dakota. Among these 12 sites, 118 different pesticides met the selection criteria. Much of these data were collected between 1993 and 1995 as part of the Red River National Water Quality Assessment (NAWQA) study. Results from that study are presented in Tornes and others (1997). Of the 118 different pesticides, for the 12 sites that met the selection criteria, only 37 pesticides had concentrations that exceeded their respective reporting levels. Twenty-five of the 37 pesticides had more than 90 percent of their data censored at the highest reporting level. The 11 pesticides detected most often are listed in table 5.

Of the pesticides in table 5, de-ethylatrazine, metolachlor, and triallate were detected most frequently in surface water in the Red River Basin based on results in the USGS NWIS data base. The pesticide metabolite de-ethylatrazine was measured at concentrations greater than the reporting level 62 percent of the time (89 of 144 samples, table 5). Metolachlor and triallate were measured at concentrations greater than the reporting level 57 and 47 percent of the time, respectively.

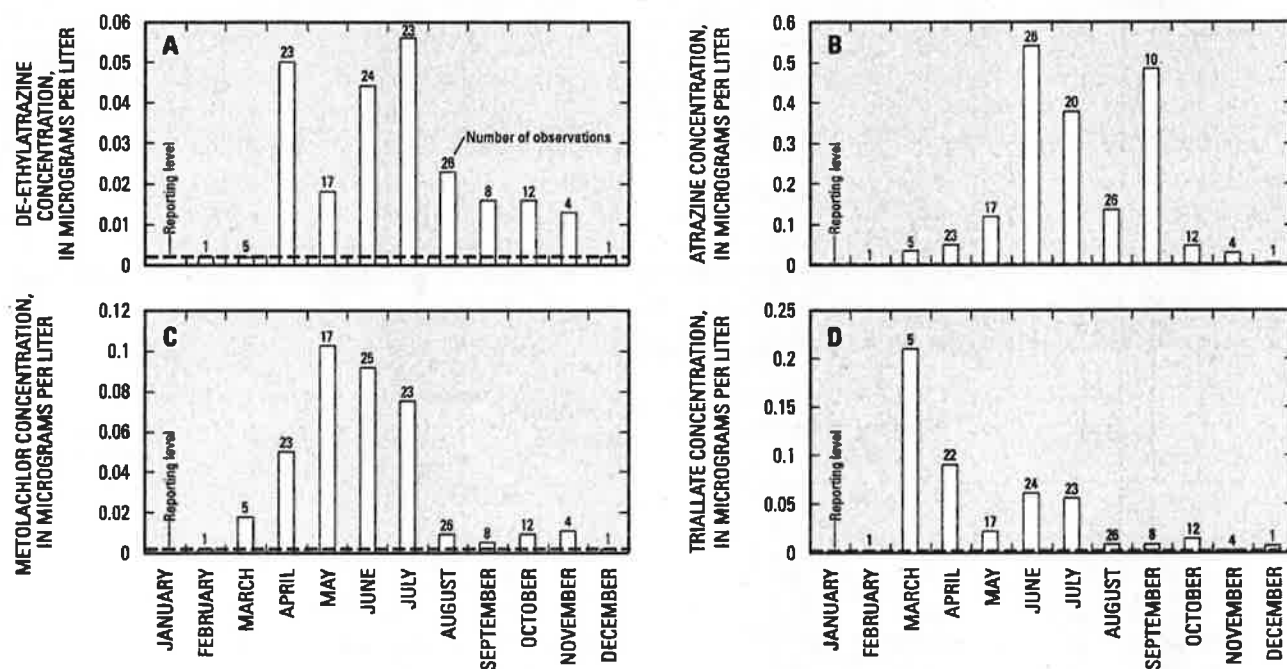
Of the 12 sites that met selection criteria for any pesticide, 5 sites met the selection criteria for de-ethylatrazine, metolachlor, and triallate; 1 site was on the Red River, 2 sites were in Minnesota, and 2 sites were in North Dakota. All of the samples were collected between 1993 and 2000. The highest de-ethylatrazine and metolachlor concentrations were detected at Red River at Pembina (site 47, fig. 3). The highest triallate concentrations, however, were in samples from the Wild Rice River at Twin Valley (site 25, fig. 3). The Wild Rice River drains areas of woodland and cropland in the Moraine (fig. 2). Triallate is a pesticide that is typically used on barley, flax, and wheat (table 2) and it is applied more extensively in North Dakota than in Minnesota. Therefore, the high concentrations in the Wild Rice watershed were not expected.

The five USGS sites that met selection criteria were combined to determine if concentrations of de-ethylatrazine, atrazine, metolachlor, and triallate showed seasonal patterns. Atrazine was included for comparison to its metabolite, de-ethylatrazine. Most pesticides are detected during the spring, with the exception of atrazine, which had the highest concentrations during summer and early fall (fig. 12). Atrazine is typically applied in spring when crops are planted (Christensen and Ziegler, 1998). Because atrazine is applied mostly to corn, the timing and method of application is likely different than

Table 5. Summary of the most frequently detected pesticides from 12 surface-water sites in the Red River of the North Basin, 1990–2004.

[U.S. Geological Survey data from National Water Information System; µg/L, micrograms per liter; <, less than]

Pesticide	Concentration range (µg/L)	Median reported concentration (µg/L)	Number of observations greater than reporting level	Number of observations
Acetochlor	<0.002–0.585	<0.002	14	90
Alachlor	<0.002–0.284	<0.002	16	145
Atrazine	<0.001–0.54	0.016	19	145
Cyanazine	<0.004–0.25	<0.004	47	144
De-ethylatrazine	<0.002–0.056	0.004	89	144
EPTC	<0.002–0.488	<0.002	54	143
Metolachlor	<0.002–0.103	0.004	83	145
Simazine	<0.005–0.07	<0.005	18	144
Triallate	<0.001–0.21	<0.001	67	143
Triazine ¹	<0.1–0.7	<0.1	13	67
Trifluralin	<0.002–0.132	<0.002	54	143

¹Triazines are a group of pesticides, which include atrazine, cyanazine, and simazine.**Figure 12.** Monthly distribution of pesticide concentrations for five selected U.S. Geological Survey stream sites (1990–2004): (A) de-ethylatrazine, (B) atrazine, (C) metolachlor, and (D) triallate.

those for metolachlor and triallate, which are applied to other crops (table 2). In addition, physical factors, including the timing of the runoff and atrazine application, tillage type, amount of atrazine applied, and other land management techniques, may cause a difference in when high atrazine concentrations are detected (Christensen and Ziegler, 1998).

The STORET data base was searched for all 115 pesticides reported in table 2. In addition, STORET was searched for triazine compounds, which are a group of chemicals that include atrazine, cyanazine, and simazine. Analytical results for sites in the Red River Basin were available for 32 of the pesticides. Of these 32 pesticides, only censored values were reported for 20 of them. For the remaining 12 pesticides, very few concentrations were at or exceeded the detection limit. Only three pesticides, 2,4-D, bentazon, and picloram, were detected more than 10 percent of the time at concentrations that exceeded the detection limit. However, these three pesticides were not detected at any site that met the minimum selection criteria. Atrazine, cyanazine, and metolachlor were detected at three sites that met the selection criteria, but few of these detections were greater than the detection limit.

The pesticides 2,4-D, bentazon, and picloram were reported most frequently in samples in the STORET data base, but de-ethylatrazine, metolachlor, and triallate were reported most frequently in samples in the USGS NWIS data base. The North Dakota Department of Health collects many of the samples from North Dakota sites reported in STORET. Many of the sites and constituents sampled are based on routine monitoring for chemical constituents that are a concern. Most of the USGS NWIS pesticide data is the result of the 1993–95 Red River NAWQA study (Tornes and others, 1997) and included a broad range of chemical analyses. The differences in the most frequently detected pesticides between the two data bases may be because of the differences in sites sampled, dates sampled, laboratory methods, and the schedule of pesticide analyses that

were determined. The differences also may be because of the difference in reporting levels and detection limits used by the different agencies.

Ground Water

Pesticide data for ground water in NWIS from 1990 through 2004 was widely distributed and denser than for 1970–1990. Ninety-nine wells were sampled in North Dakota and 157 wells were sampled in Minnesota for 1990–2004. Results for 156 pesticides were available for 1990–2004 in the NWIS data base. All concentrations were less than the reporting level for 127 pesticides. Of the remaining 29 pesticides, only 5 had more than 10 percent of values that exceeded their respective reporting level.

The chemicals that were detected most frequently were alachlor ethanesulfonic acid (ESA), atrazine, de-ethylatrazine, picloram, and triazine (table 6). Alachlor ESA is a metabolite of alachlor; de-ethylatrazine is a metabolite of atrazine; and triazine is a group of pesticides, which includes atrazine. Alachlor ESA concentrations ranged from less than 0.02 to 0.96 $\mu\text{g/L}$; atrazine concentrations ranged from less than 0.001 to 0.54 $\mu\text{g/L}$; de-ethylatrazine concentrations ranged from less than 0.002 to 1.9 $\mu\text{g/L}$; picloram concentrations ranged from less than 0.01 to 0.02 $\mu\text{g/L}$; and triazine concentrations ranged from less than 0.1 to 3 $\mu\text{g/L}$ (table 6).

The chemicals that were detected most frequently in ground water showed consistent patterns of detection. Only alachlor ESA and picloram were detected in samples from Polk County, Minn., wells; the highest concentrations of atrazine, de-ethylatrazine, and triazine were in samples from Otter Tail County, Minn., wells. Aquifers in areas of high soil permeability may be susceptible to contamination because of the downward movement of pesticides.

Table 6. Summary of the most frequently detected pesticides in ground water from 263 sites in the Red River of the North Basin, 1990–2004.

[U.S. Geological Survey data from National Water Information System; $\mu\text{g/L}$, micrograms per liter; ESA, ethanesulfonic acid; <, less than]

Pesticide	Concentration range ($\mu\text{g/L}$)	Median reported concentration ($\mu\text{g/L}$)	Number of observations greater than reporting level	Number of observations
Alachlor ESA	<0.02–0.96	<0.02	10	61
Atrazine	<0.001–0.54	0.007	58	286
De-ethylatrazine	<0.002–1.9	0.006	13	285
Picloram	<0.01–0.02	<0.01	2	10
Triazine ¹	<0.1–3	<0.1	8	69

¹Triazines are a group of pesticides, which include atrazine, cyanazine, and simazine.

Of the pesticides most frequently detected, only atrazine and picloram have MCLs established by the USEPA (U.S. Environmental Protection Agency, 1996). One of 285 samples exceeded the atrazine MCL of 3 µg/L. None of the 11 picloram samples exceeded the MCL of 0.5 µg/L.

There are few similarities between the most applied pesticides in Minnesota and North Dakota (table 2) and the most detected pesticides in the Red River Basin. This may be partially because table 2 includes all of the treated acreage, and thus, all of the basins in Minnesota and North Dakota, whereas tables 5 and 6 include only the Red River Basin. Crops grown and pesticides used in the Red River Basin are different than in the two States as a whole. Additionally, some pesticides, such as glyphosate, that were applied were not analyzed during 1990–2004 in the Red River Basin by the agencies that report data in NWIS or STORET.

Aside from the USGS NWIS data base, very little data existed for pesticides in ground water. STORET did not have ground-water data for most pesticides and the ND SWC also did not have ground-water pesticide data in their on-line data base. The MDA tested 18 ground water wells across Minnesota during 2004 for 21 pesticides or pesticide metabolites (electronic data from Catherine O'Dell, Minnesota Pollution Control Agency, August 30, 2006). Fourteen of the 21 pesticides were not detected in any well. Acetochlor oxanilic acid (OXA) and atrazine were each detected in one well. Acetochlor ESA, de-ethylatrazine, and metolachlor OXA each were detected in two wells. Alachlor ESA was detected in 5 of 18 wells with an average concentration of 0.14 µg/L, and metolachlor ESA was detected in 4 of 18 wells with an average concentration of 0.19 µg/L.

Comparison to Historical Data

Because this report is an update of the 1994 report by Tornes and Brigham, an attempt is made here to compare data from the 1970–1990 reporting period to that from the 1990–2004 reporting period. However, sampling schemes, methods, and sites sampled and median annual streamflow are different between the two reporting periods; therefore, a comparison of water-quality is difficult. Generally, however, a few consistencies and differences were evident.

For nitrogen compounds, samples from Pembina River surface-water sites had the highest nitrite plus nitrate concentrations during both reporting periods. However, TKN concentrations also were high at these sites when compared to other Red River Basin sites during 1970–90; whereas TKN

concentrations at Pembina River sites during 1990–2004 were not substantially different than concentrations at other sites in the basin. During 1970–90 total phosphorus concentrations generally were highest at Red River sites, whereas during 1990–2004 total phosphorus concentrations generally were highest at Pembina River sites.

During 1970–90, three counties in North Dakota, Barnes, Griggs, and Steele, and only Otter Tail County in Minnesota had wells with nitrate concentrations greater than the 10 mg/L MCL. During 1990–2004, 18 counties in North Dakota and five counties in Minnesota had wells with nitrate concentrations greater than the MCL. However, considerably more samples were collected during 1990–2004 than during 1970–90, thus making the probability of detecting concentrations that exceeded the MCL greater during 1990–2004.

For SSC, only 13 sites had sufficient data during 1970–90 (Tornes and Brigham, 1994, fig. 20), whereas data were available for 43 sites during 1990–2004 (figs. 10 and 11). Pembina River sites had high SSC relative to other sites during both reporting periods.

The most notable differences between the two reporting periods were for pesticides. This is because samples were analyzed for different pesticides during the two reporting periods and because different pesticides were detected. Different pesticides were in the data bases for a number of reasons, including changes in the crops grown, the availability and use of newly developed pesticides, the banning of some pesticides, and the loss of favor of some pesticides among farmers. Of the pesticides that were analyzed during both reporting periods, different pesticides were detected, in part, because of changes in analytical methods and reporting levels.

When research supports the negative effects of certain pesticides on human health and wildlife, the USEPA acts to ban the pesticides. Since the Federal Environmental Pesticide Control Act was implemented in 1972, certain pesticides have continued to be added to the list beginning with the banning of DDT in 1972. The banning of certain pesticides affects what chemicals are detected in water and also affects the differences between the historical data (Tornes and Brigham, 1994) and the data presented in this report.

None of the most frequently detected pesticides for which water samples were collected and analyzed by the USGS during 1970–90 were detected frequently during 1990–2004. Only one pesticide, 2,4-D, was detected in more than 10 percent of surface-water samples that were analyzed during the 1970–90 reporting period, compared to 11 pesticides, shown in table 5, that were detected in more than 10 percent of the samples analyzed during 1990–2004.

Summary

Nutrient, suspended sediment, and pesticide data from 1990–2004 from the Red River of the North was compiled and summarized in this report, which serves as an update to the report, *Nutrients, suspended sediment, and pesticides in waters of the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1970–90*. Water quality continues to be a concern for this mainly agricultural basin, and, therefore, the U.S. Geological Survey (USGS) and the Minnesota Pollution Control Agency (MPCA) cooperated to provide this update.

The Red River Basin is divided into the four physiographic areas, the Drift Prairie, Red River Valley Lake Plain, Lake-Washed Till Plain, and Moraine, based on topography and soils. These physiographic areas have some bearing on land use and, therefore, may be related to water quality. Sixty-six percent of the agricultural land in the basin is cropland. Nutrients and pesticides are applied to most of the crops in an effort to maximize production.

Fertilizer applications are greatest in Polk County, Minn. and Cass County, N. Dak., both of which border the main stem of the Red River. Manure application is greatest in Otter Tail County, Minn. Pesticides applied in the greatest abundance in Minnesota and North Dakota are 2,4-D, MCPA, and dicamba.

Streamflow varied widely throughout the basin during the 1990–2004 study period. For 19 of 22 streamflow sites, median annual streamflow during the study period exceeded the long-term average streamflow for the period of record at those sites. Streamflow at all four main-stem Red River sites exceeded long term average streamflows. High streamflows have substantial effect on water quality, especially in the spring when agricultural chemicals are applied and when there is no crop cover to hold the soil in place.

Although nutrients occur naturally in the environment, agricultural practices can increase their transport to natural waters, and transport may increase during storms. Nitrite plus nitrate concentrations ranged from 0.02 to 5.2 milligrams per liter at 23 USGS stream sampling sites and from less than 0.005 to 7.7 milligrams per liter at 23 USEPA STORET stream sites. Stream sites on the Pembina River, that drain a watershed mainly in the Drift Prairie physiographic area, had the highest nitrite plus nitrate concentrations compared to other Red River Basin sites. All nitrite plus nitrate concentrations at USGS stream sites included in this report during 1990 through 2004 were less than the USEPA drinking water standard of 10 milligrams per liter. Total Kjeldahl nitrogen concentrations at USGS stream sites ranged from 0.1 to 7.5 milligrams per liter, whereas STORET stream sites had total Kjeldahl nitrogen concentrations ranging from 0.234 to 2.38 milligrams per liter.

Total phosphorus concentrations ranged from less than 0.005 to 4.14 milligrams per liter for USGS stream sites and from less than 0.018 to 1.44 mg/L for STORET stream sites. Pembina River sites had higher total phosphorus concentrations than surrounding sites. Soil characteristics or agricultural practices may cause more phosphorus to be transported to the

streams in the Drift Prairie physiographic area than to other streams. Dissolved phosphorus data were presented for USGS sites only, and concentrations ranged from 0.003 to 4.13 milligrams per liter; dissolved phosphorus concentrations were highest in samples from the Bois de Sioux and Pembina River sites.

Ground-water samples for nutrients also were collected and measured by a number of agencies in the basin and are compiled and summarized in this report. The number of wells sampled in each county varied greatly and ranged from zero to more than 300.

Reported nitrate concentrations in ground water from North Dakota counties ranged from less than 0.023 to 113 milligrams per liter during 1990–2004. Sheridan County, in the Drift Prairie physiographic area, had the highest ground-water nitrate concentrations when compared to other well sites on the North Dakota side of the basin. Nitrate concentrations in ground water from Minnesota counties ranged from less than 0.005 to 133 milligrams per liter. The highest concentrations were in samples from in the Lake-Washed Till Plain and Moraine physiographic areas. Marshall and Otter Tail Counties in Minnesota had high fertilizer applications relative to other Minnesota counties in 2002, which may explain high nitrate concentrations in ground water; however, Sheridan County in North Dakota did not have high fertilizer application rates in 2002 compared to other North Dakota and Minnesota counties. Although there appeared to be a correlation between fertilizer applications and ground water nitrate concentrations in Minnesota counties, there appeared to be little correlation between fertilizer applications and nitrate concentrations in ground water in North Dakota counties.

Suspended-sediment data were available for 48 surface-water sites in Minnesota, 31 sites in North Dakota, and 10 main-stem Red River sites. Median suspended-sediment concentrations ranged from about 4 to 706 milligrams per liter. The highest concentrations occurred in samples from the Pembina River, which is located in northern North Dakota in the Red River Valley Lake Plain and drains part of the Drift Prairie.

Pesticide data from 12 USGS stream sites in the Red River Basin were examined. Most of the 118 chemicals for which analyses were performed were either not detected in any sample or occurred below their respective reporting limits. De-ethylatrazine, which is a metabolite of atrazine, metolachlor, and triallate were detected most frequently at USGS stream sites. The highest de-ethylatrazine and metolachlor concentrations were detected at the Red River at Pembina. The highest triallate concentrations were detected at Wild Rice River at Twin Valley. The highest concentrations of these three pesticides were detected during the spring, in contrast to atrazine, for which the highest concentrations were detected during summer and early fall.

Some surface-water pesticide data were available in STORET. The most frequently detected pesticides for Red

River Basin sites in the STORET data base were 2,4-D, bentazon, and picloram.

The pesticide compounds detected most frequently in ground water were alachlor ESA, atrazine, de-ethylatrazine, picloram, and triazine at USGS-sampled well sites. Very little ground-water data were available from STORET. The USEPA has established MCLs for atrazine and picloram in drinking water of 0.003 and 0.5 milligrams per liter, respectively. None of the 11 picloram results exceeded this level, and one of the 285 ground-water atrazine samples exceeded the MCL.

When a comparison was made with the data presented in this report for 1990–2004 and the historical data during 1970–90, a few similarities as well as differences are evident. Pembina River surface-water sites continued to have the highest nitrite plus nitrate and suspended-sediment concentrations during the 1990–2004 time period. However, the Pembina River also had the highest total phosphorus concentrations for 1990–2004, in contrast to 1970–90, when Red River sites generally had the higher total phosphorus concentrations than Pembina River sites.

The most notable differences between the two reporting periods were seen in the pesticides, partly because different pesticides were analyzed during 1970–90 and 1990–2004. None of the most frequently detected pesticides or metabolites sampled and analyzed by the U.S. Geological Survey or available in STORET during 1990–2004 were detected frequently during 1970–90, with the exception of 2,4-D.

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